

TECHNICAL REPORT BRL-TR-3402

# BRL

# THERMAL DECOMPOSITION OF HNIW AND HNIW-BASED FORMULATIONS

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SEPTEMBER 1992



U.S. ARMY LABORATORY COMMAND

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# REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188



| 1. AGENCY USE ONLY (Leave blank) | 2. REPORT DATE | 3. REPORT TYPE AND DATES COVERED |
|---|---|---|
| | September 1992 | Final, Aug 91 - Nov 91 |

**4. TITLE AND SUBTITLE**
Thermal Decomposition of HNIW and HNIW-Based Formulations

**5. FUNDING NUMBERS**
PR: 1L161102AH43

**6. AUTHOR(S)**
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**7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)**

**8. PERFORMING ORGANIZATION REPORT NUMBER**

**9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)**
U.S. Army Ballistic Research Laboratory
ATTN: SLCBR-DD-T
Aberdeen Proving Ground, MD 21005-5066

**10. SPONSORING / MONITORING AGENCY REPORT NUMBER**
BRL-TR-3402

**11. SUPPLEMENTARY NOTES**
*CCS Instruments Systems, Inc., Avondale, PA

**12a. DISTRIBUTION / AVAILABILITY STATEMENT**
Approved for public release; distribution is unlimited.

**12b. DISTRIBUTION CODE**

**13. ABSTRACT** *(Maximum 200 words)*

The pyrolytic decomposition of hexanitrohexazaisowurtzitane (HNIW) and a HNIW-based propellant formulation were investigated using several infrared and mass spectrometric techniques. The pyrolysis product distributions of HNIW (500° C and 1,000° C pyrolysis) were compared to those of HMX and RDX. At both temperatures, HNIW produced a higher $CO_2$:$N_2O$ ratio than did HMX or RDX. Several products were generated by all three nitramines, while others were unique to HNIW. When heated under vacuum conditions, HMX appears to undergo both vaporization and decomposition, while HNIW appears to remain in the condensed phase prior to rapid decomposition. Investigation of the effect of propellant ingredients (i.e., nitrate ester plasticizers and a modified DuPont HYCAR thermoplastic elastomer) on the pyrolysis product distribution of a HNIW-based propellant indicates the "removal" of several HNIW decomposition products by those ingredients. Desorption studies indicate possible evaporation and/or decomposition of nitrate ester plasticizers in "aged" HNIW/TPE propellants. Observed variations in the pyrolysis product distribution as a function of sample size are attributed to as yet unidentified secondary reactions.

| 14. SUBJECT TERMS | 15. NUMBER OF PAGES |
|---|---|
| HNIW, Hexanitrohexazaisowurtzitane, pyrolysis, thermal decomposition, nitramines | 36 |
| | 16. PRICE CODE |

| 17. SECURITY CLASSIFICATION OF REPORT | 18. SECURITY CLASSIFICATION OF THIS PAGE | 19. SECURITY CLASSIFICATION OF ABSTRACT | 20. LIMITATION OF ABSTRACT |
|---|---|---|---|
| UNCLASSIFIED | UNCLASSIFIED | UNCLASSIFIED | UL |

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ACKNOWLEDGMENT

We thank Rod Willer of Thiokol Corporation (Elkton Division) for providing samples of HNIW, a modified DuPont HYTREL thermoplastic elastomer (TPE), and a plasticized HNIW/TPE propellant formulation for use in this study.

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# 1. INTRODUCTION

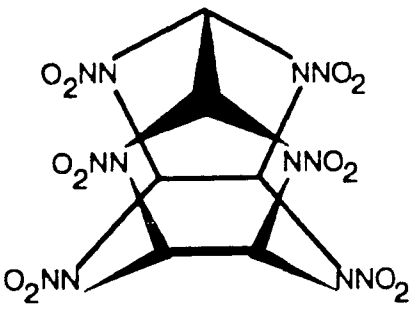
There are two general reasons for studying the thermochemistry of energetic materials and propellant formulations based on them. First, short term benefits can be achieved if correlations can be established between measured thermochemical behavior (e.g., pyrolysis product distributions) and performance properties (e.g., ignitability, sensitivity, burning rate) of formulations (Fifer et al. 1991a); such correlations can form the basis for small-scale screening tests for the property of interest, as well as provide formulation guidelines to replace costly and time-consuming trial-and-error techniques. Second, measurements of kinetics and mechanisms provide the input needed for the development of detailed ignition and combustion models (Schroeder 1982, 1984a, 1984b, 1985a, 1985b; Fifer 1984; Boggs 1984). For example, pyrolysis studies provide data directly relevant to certain phases of the ignition process and also complement the very difficult near-surface combustion diagnostics in providing detailed information about the boundary conditions for the gas-phase flame (species leaving the surface). Similarly, extinguished propellant studies provide a way to investigate the extent and nature of the condensed phase chemistry taking place during combustion, providing input to combustion models.

In studying the thermochemistry of energetic materials and propellant formulations, we have pioneered the first use of a number of experimental techniques, including pyrolysis gas chromatography-Fourier transform infrared (P-GC-FTIR) spectroscopy (Fifer et al. 1985; Liebman et al. 1986; Kaste 1988), pyrolysis triple quadrupole mass spectrometry (P-TQMS) (Liebman et al. 1987; Snyder et al. 1989, 1990, to be published), liquid chromatography-mass spectrometry (LC-MS) (Snyder et al. 1991), the use of trapping/ concentrator systems in conjunction with pyrolysis gas chromatography (P-GC) (Fifer et al. 1985; Liebman et al. 1986), P-GC-FTIR (Fifer et al. 1985; Liebman et al. 1986), or P-GC-MS (Schroeder 1990a), and the use of FTIR-photoacoustic spectroscopy (FTIR-PAS) (Pesce-Rodriguez and Fifer 1991; Schroeder et al. 1991) and FTIR-Microscopy (Pesce-Rodriguez and Fifer 1992; Pesce-Rodriguez et al., to be published) (FTIR-Mic) for characterization of propellant surfaces and residues. In addition, we have been among the first to use capillary GC techniques instead of the more commonly used packed GC columns, permitting larger pyrolysis products (e.g., amides, aldehydes, ketones, etc.) to be observed instead of only the predominant permanent gases (e.g., CO, $CO_2$, $H_2O$, $N_2$, NO, $NO_2$, $N_2O$). When seeking pyrolysis-performance correlations, the rationale for the use of these various techniques has in most cases been to increase the "information content" of the pyrolysis experiment. That is, we believe one is more likely to find a correlation between pyrolysis products and performance test data if, say, 30 or 40 products are measured instead of only 4 or 5. Also, when seeking mechanistic information, the larger pyrolysis

fragments are much more likely to provide information about the early steps in the decomposition chemistry than are the small permanent gas type molecules which may be formed primarily toward the end of the sequence of chemical events. However, there are additional reasons for using some of these techniques. For example, the use of trapping/concentrator techniques permits the pyrolysis experiment to be carried out in air or other atmospheres, rather than only in the GC carrier gas (usually helium), and the use of tandem mass spectrometric ("MS/MS") techniques such as TQMS permits separation and identification of products while retaining the temporal information (i.e., the order of evolution of the products) that is lost when using chromatographic techniques.

## 2. EXPERIMENTAL

2.1 Samples. Samples of hexanitrohexazaisowurtitane (HNIW, structure given below), modified DuPont HYTREL thermoplastic elastomer (TPE), and a plasticized HNIW/TPE propellant formulation were provided by Rod Willer of Thiokol Corporation, Elkton Division. FTIR analysis of the HNIW showed it to be the β polymorph (see Nielsen et al. [1989] for FTIR spectra of the various polymorphs). The sample had a fine particle size (~2–4 μm) and was shown by TGA to have a decomposition temperature of ~220° C. The propellant formulation was composed of HNIW, a modified HYTREL TPE, and nitrate ester plasticizers. In addition to the Thiokol plasticized HNIW/TPE formulation, a hand-mixed, unplasticized formulation was prepared by the authors and also examined (extinguished propellant study only). This hand-mixed sample was prepared by melting 1.2 g of the modified HYTREL TPE in an agate mortar. The TPE was melted and kept in the molten state by means of a hot plate and a heat lamp. To the molten thermoplastic, 1.6 g HNIW were then added in four equivalent portions, mixing thoroughly before the addition of the next portion. The propellant mixture was then rolled into a cylinder and allowed to cool. For extinguished propellant studies, the sample was burned at atmospheric pressure, and extinguished by dropping into a container of water.




Hexanitrohexazaisowurtitane (HNIW)

2.2 Pyrolysis—Gas Chromatography—FTIR (P-GC-FTIR). Instrument configuration: CDS (Avondale, PA) Model 122 Pyroprobe (coil probe, sample in quartz capillary) connected via a heated interface chamber to the splitless injector of a HP 5890 GC; outlet of the capillary column connected to the light pipe of a Hewlett Packard (HP, Palo Alto, CA) Model 5965 IRD dedicated FTIR detector with a narrow band mercury cadmium telluride (MCT) detector. GC conditions: Quadrex capillary column, 0.32-mm × 25-m × 3-μm OV-17 film, programmed as follows: 50° C for 3 min, 50 to 200° C at 10°/min. Injector and interface chamber held at 200° C; light pipe held at 200° C. Unless otherwise noted (as in Section 3.1.1), splitless GC injector valves were opened at the initiation of the pyrolysis pulse. FTIR conditions: three interferograms per second were continuously collected at 8 $cm^{-1}$ resolution during the chromatographic run. Real-time chromatograms were recorded via application of the Gram-Schmidt algorithm (Griffiths and de Haseth 1986), which constructs chromatograms based on infrared response vs. time. Associated FTIR spectra for each recorded chromatographic peak were available for interpretation or for automated search of the EPA library of approximately 5,000 vapor phase spectra.

Individual permanent gases are not separated by capillary columns and elute as a single chromatographic peak. Comparison of the relative quantities of permanent gases generated by different samples was accomplished by examination of the FTIR spectrum associated with that peak and measuring the relative intensity of the strongest absorbance band for each gas in that spectrum (i.e., $CO_2$, 2,363 $cm^{-1}$; $N_2O$, 2,238 $cm^{-1}$; CO, 2,111 $cm^{-1}$, NO, 1,912 $cm^{-1}$).

2.3 Pyrolysis—Fourier Transform Infrared (P-FTIR) Spectroscopy. A Barnes (Stamford, CT) Pyrolyzer and Mattson (Madison, WI) Polaris FTIR with liquid nitrogen-cooled MCT detector were used. The pyrolyzer is designed such that when placed in the spectrometer sample compartment, pyrolysis gases are evolved directly into the IR beam. Typical conditions involved 16 scans at 2 $cm^{-1}$ resolution recorded immediately after pulse pyrolysis at 450° C or 1,300° C (in air or nitrogen); additional spectra were recorded over a several-minute period following pyrolysis.

2.4 Pyrolysis—Gas Chromatography—Mass Spectrometry (P-GC-MS). Instrument configuration was as follows: CDS Model 122 Pyroprobe (coil probe, sample in quartz capillary) connected via a heated interface chamber to the injector of a HP 5890 GC, which in turn was connected via a heated transfer line to a Finnigan (San Jose, CA) Incos 50 quadrupole mass spectrometer. GC conditions: HP-1 capillary column, 0.2-mm × 12-m × 0.33-μm cross-linked methyl silicone, programmed as follows: −50° C for 3 min, −50° C to 280° C at 25°/min, hold 3 min. Interface chamber held at 150° C; injector and transfer

line at 200° C. MS conditions: 70-eV ionization, mass range 20–500 amu scanned every 0.33 s. Pulse pyrolysis in helium at 500° C or 1,000° C. The software produces a total ion chromatogram, corresponding peak area tables with the mass spectrum available for any observed peak, and automated searches of the National Institute of Standards and Technology (NIST) library of approximately 50,000 mass spectra.

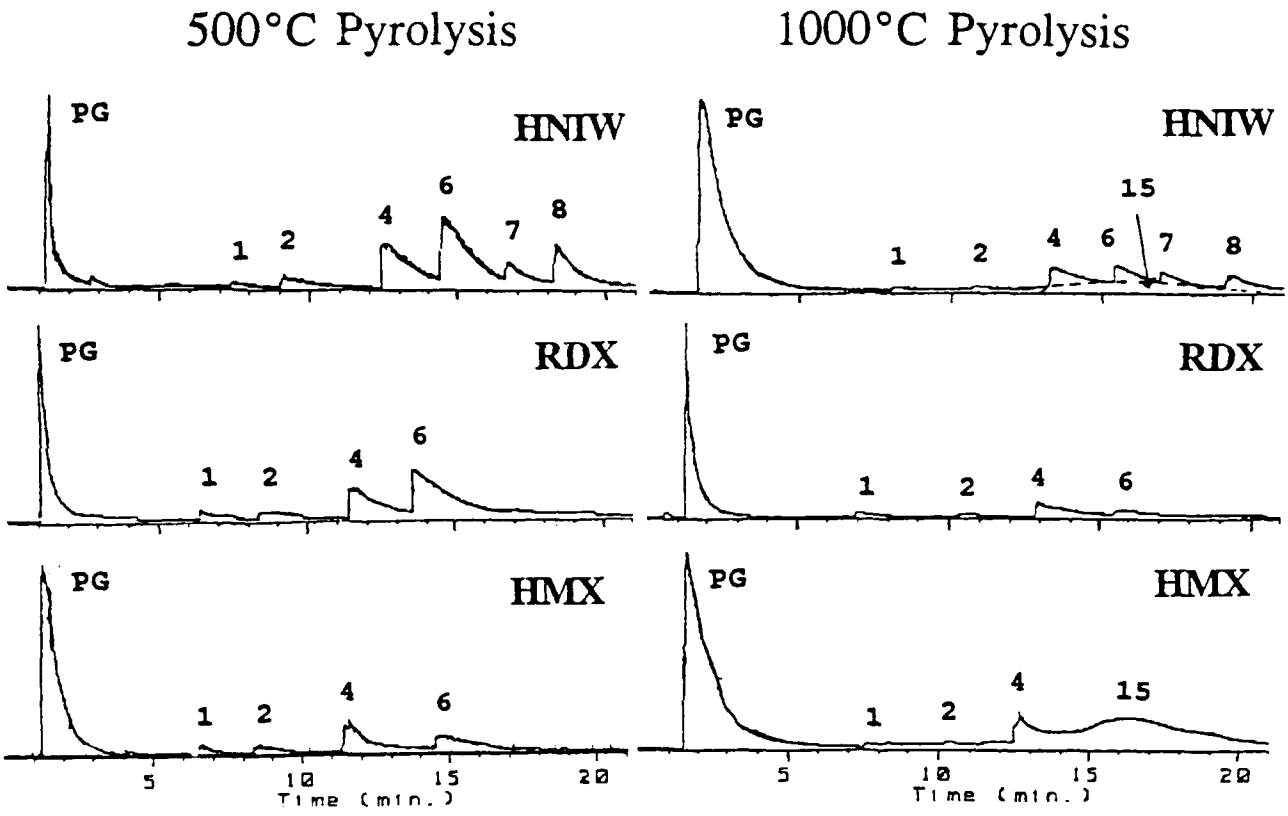
2.5 Pyrolysis/Thermolysis—Mass Spectrometry (P-MS). As with the P-FTIR technique, there is no chromatograph involved in P-MS, so temporal information can be obtained. Samples were analyzed on a Finnigan Model 4500 TSQ triple quadrupole system, operated using only the first quadrupole and with standard 70-eV electron ionization. Samples were placed in a quartz capillary tube and heated by a CDS Model 122 Pyroprobe with a direct insertion probe (DIP) inserted directly into the ionization chamber of the MS. Isothermal, programmed (30°/min and 60°/min), and pulsed (at 1,000° C and 1,200° C) heating were employed. Mass spectra were scanned over the mass-to-charge (m/z) range of 45–650 every second for up to several minutes. Instrument software permits display of total- or selected-ion traces vs. time, as well as the corresponding mass spectrum at any point in the event.

2.6 Photoacoustic—FTIR (PA-FTIR) Spectroscopy. Spectra were obtained on the Mattson Polaris spectrometer described in Section 2.3. Detection of the photoacoustic signal was achieved with a helium-purged MTEC Model 100 photoacoustic cell. Each spectrum was the average of 32 scans with a resolution of 32 $cm^{-1}$. Spectra were obtained with a moving mirror velocity of 0.316 cm/s and were ratioed against a carbon black (Norit-A) background.

## 3. RESULTS

### 3.1 P-GC-FTIR Spectroscopy.

3.1.1 Comparison of Pyrolysis Product Distributions of HNIW, RDX, and HMX. Figure 1 shows chromatograms generated by pyrolysis of HNIW, RDX, and HMX at 500° C and 1,000° C. In all chromatograms, there is large peak due to unseparated permanent gases near the beginning of the chromatogram, followed by a series of peaks due to larger products extending out to retention times of approximately 20 min. Infrared spectra of larger products can be found in the appendix of this report. Uncalibrated, relative absorbances obtained from IR spectra associated with the permanent gas chromatographic peaks of HNIW, RDX, and HMX are given in Table 1. (When examining the data in




Note: PG: permanent gases
1: triazine 6: ester
2: formic acid 7: N-C heterocycle
4: formamide 8: N-C heterocycle

Figure 1. P-GC-FTIR Data for HNIW, RDX, and HMX Pyrolyzed at 500° C and 1,000° C. Sample Size: 2 mg. (GC Injector Valve Opened at Termination of Pyrolysis Pulse).

Table 1. Individual Permanent Gas Products Obtained on Pyrolysis of HNIW, RDX, and HMX

| Assignment | 500° C Pyrolysis | | | 1,000° C Pyrolysis | | |
|---|---|---|---|---|---|---|
| | HNIW | RDX | HMX | HNIW | RDX | HMX |
| | (relative IR intensity) | | | (relative IR intensity) | | |
| $CO_2$ | 1.00 | 0.40 | 0.52 | 1.00 | 1.00 | 1.00 |
| $N_2O$ | 0.56 | 1.00 | 1.00 | 0.12 | 0.84 | 1.00 |
| CO | 0.08 | 0.04 | 0.08 | 0.04 | 0.08 | 0.12 |
| NO | 0.16 | 0.10 | 0.12 | 0.04 | 0.12 | 0.16 |

this table, the reader is advised against comparing absorbance values of $CO_2$ and $N_2O$, which absorb strongly in the infrared, with those of CO and NO, which absorb weakly.) On inspection of this table, it is observed that while both RDX and HMX generate relatively more $N_2O$ than $CO_2$ when pyrolyzed at 500° C, HNIW generates more $CO_2$ than $N_2O$ at that temperature. When pyrolyzed at 1,000° C, both RDX and HMX generate relatively more $N_2O$ than does HNIW; all three oxidizers generate relatively high levels of $CO_2$. There is no obvious trend in the production of CO and NO other than that HNIW appears to generate relatively less CO and NO than do RDX and HMX when pyrolyzed at 1,000° C.

Area-percents calculated from chromatograms of HNIW, RDX, and HMX are given in Table 2. As a result of two changes in experimental procedure, values in both tables differ from those reported in earlier works (Pesce-Rodriguez, Shaw, and Fifer 1991; Shaw and Fifer 1988; Pesce-Rodriguez et al. 1991; Fifer et al. 1991b). In previous experiments, the GC interface temperature was 100° C rather than 200° C, as in these experiments. In addition, for previous experiments as well as in those of subsequent sections of this report, the splitless GC injector valve was opened at the initiation of the 20-s pyrolysis pulse, whereas the chromatograms presented in this section were obtained by opening the valve at the termination of the pyrolysis pulse. The result of the closed GC injector valve is that pyrolysis products were exposed to the pyrolysis temperature longer than in the previous experiments, in which pyrolysis products were immediately swept away from the decomposing sample and into the GC column.

As observed from Table 1 and the chromatograms in Figure 1, there are several pyrolysis products common to HNIW, RDX, and HMX, (i.e., the permanent gases, product 1 [triazine], product 2 [formic acid], product 4 [formamide], and product 6 [an ester]). In addition to these products, pyrolysis of HNIW and HMX at 1,000° C produces product 15 (an isocyanate). Only HNIW generates products 7 and 8 (nitrogen-carbon heterocycles). It is anticipated that products 4, 6, 7, 8, and 15 will be found to correspond to presently unidentified products in the P-GC-MS experiments (Section 3.3) once the data from the two techniques is correlated.

3.1.2 Effect of Sample Size on Pyrolysis Product Distribution. A comparison of the chromatograms in Figure 2 illustrates the effect of the sample size examined in P-GC-FTIR experiments. The chromatograms shown in Figure 2 are those of HNIW, though the same trend is observed for the HNIW/TPE formulation (see Figure 3). For very small samples (i.e., <1 mg, Figures 2a and 2d), the large permanent gas peak and virtual absence of larger pyrolysis products suggests that the pyrolysis process

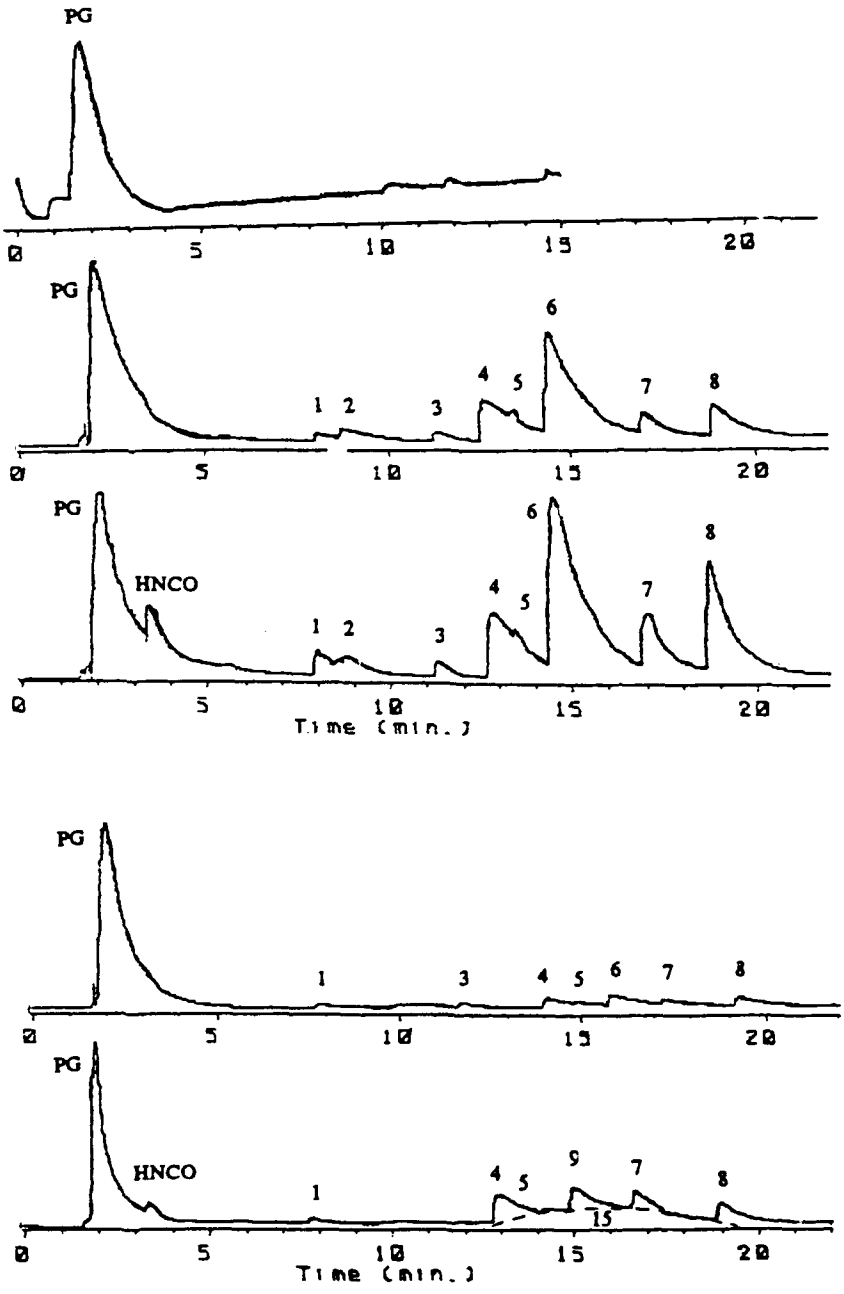
Table 2. Product Distribution for HNIW, RDX, and HMX When Pyrolyzed at 500° C and 1,000° C

| Retention Time (min) | Assignment | Product Number | 500° C Pyrolysis | | | 1,000° C Pyrolysis | | |
|---|---|---|---|---|---|---|---|---|
| | | | HNIW | RDX | HMX | HNIW | RDX | HMX |
| | | | (area-%) | | | (area-%) | | |
| 1.5 | Permanent Gases | — | 21.1 | 52.9 | 61.4 | 69.3 | 68.2 | 54.8 |
| 7.5 | Triazine | 1 | 1.6 | 4.6 | 3.2 | 0.8 | 4.3 | 0.7 |
| 10.0 | Formic Acid | 2 | 4.4 | 3.3 | 4.9 | 0.7 | 1.7 | 0.4 |
| 12.5 | Formamide | 4 | 19.5 | 18.9 | 16.5 | 3.9 | 17.1 | 4.1 |
| 15.0 | Ester(?) | 6 | 30.9 | 20.1 | 14.1 | 2.7 | 8.7 | — |
| 16.5 | Isocyanate(?) | 15 | — | — | — | 19.6 | — | 40.0 |
| 17.0 | N-C Heterocycle(?) | 7 | 7.2 | — | — | 1.9 | — | — |
| 19.0 | N-C Heterocycle(?) | 8 | 15.2 | — | — | 1.3 | — | — |

is very efficient. For large samples (i.e., ≥ 2 mg, Figures 2b, 2c, and 2e), HNCO and a significant quantity of large pyrolysis products are observed, suggesting a low efficiency pyrolysis process. These observations alert the researcher to the dangers of comparing results obtained from samples of different sizes. On a positive note, comparison of results obtained with a range of sample sizes may contribute to the understanding of differences in decomposition processes occurring in condensed vs. gas phase, early- vs. secondary-processes, etc. Investigations along that line are currently in progress. An investigation of temperature sensitivity will also be conducted to determine why products 3 and 5 are observed only when the GC injector valve opened at the initiation of the pyrolysis pulse (see Figures 2 and 3), but not when the valve is opened at the termination of the pulse (see Figure 1).

3.1.3 Effect of Propellant Ingredients on Pyrolysis Product Distribution. Chromatograms of pyrolysis products generated by the plasticized HNIW/TPE propellant formulation and unplasticized binder are given in Figures 3 and 4, respectively. Spectra of the propellant formulation pyrolysis products are given in the appendix of this report.

The propellant formulation was subjected to both desorption and pyrolysis experiments. Chromatograms obtained from desorption experiments (Figures 3a and 3b) varied over time, suggesting that "aging" had occurred. Analyses performed on receipt of the samples ( "Day 1" sample, Figure 3a)




(a) 0.5 mg pyrolyzed at 500°C

(b) 2 mg pyrolyzed at 500°C

(c) 5 mg pyrolyzed at 500°C

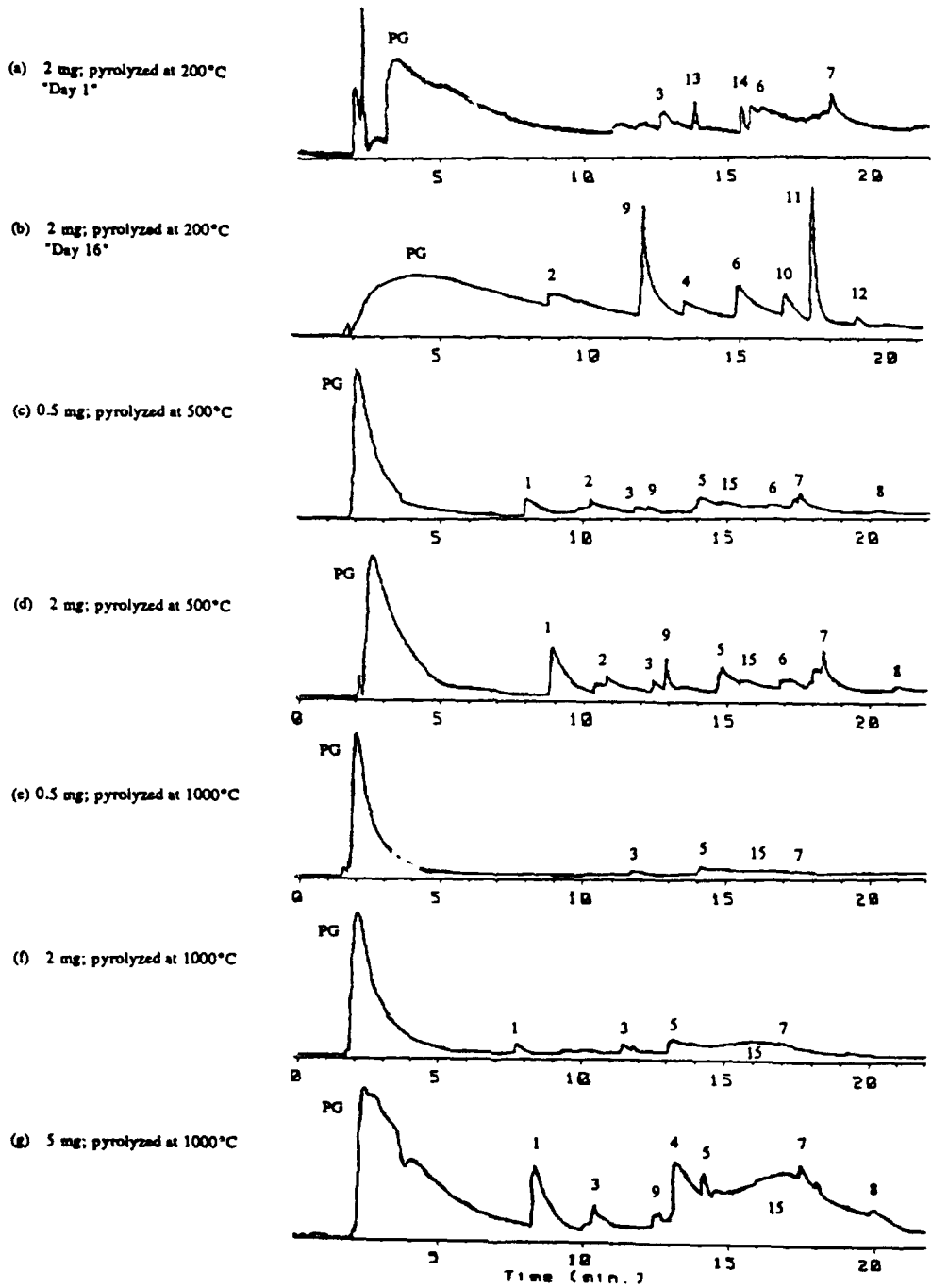
(d) 0.5 mg pyrolyzed at 1000°C

(e) 2 mg pyrolyzed at 1000°C

Note: PG: permanent gases

| | |
|---|---|
| 1: triazine | 6: ester |
| 2: formic acid | 7: N-C heterocycle |
| 4: formamide | 8: N-C heterocycle |

Figure 2. P-GC-FTIR Data for HNIW. (GC Injector Valve Opened at Initiation of Pyrolysis Pulse).




Note: PG: permanent gases

| | |
|---|---|
| 1: triazine | 5: N-C heterocycle |
| 2: formic acid | 6: ester |
| 3: carboxylic acid | 7: N-C heterocycle |
| 4: formamide | 8: N-C heterocycle |

Figure 3. P-GC-FTIR Data for Plasticized HNIW/TPE Propellant Formulation. (GC Injector Valve Opened at Initiation of Pyrolysis Pulse).

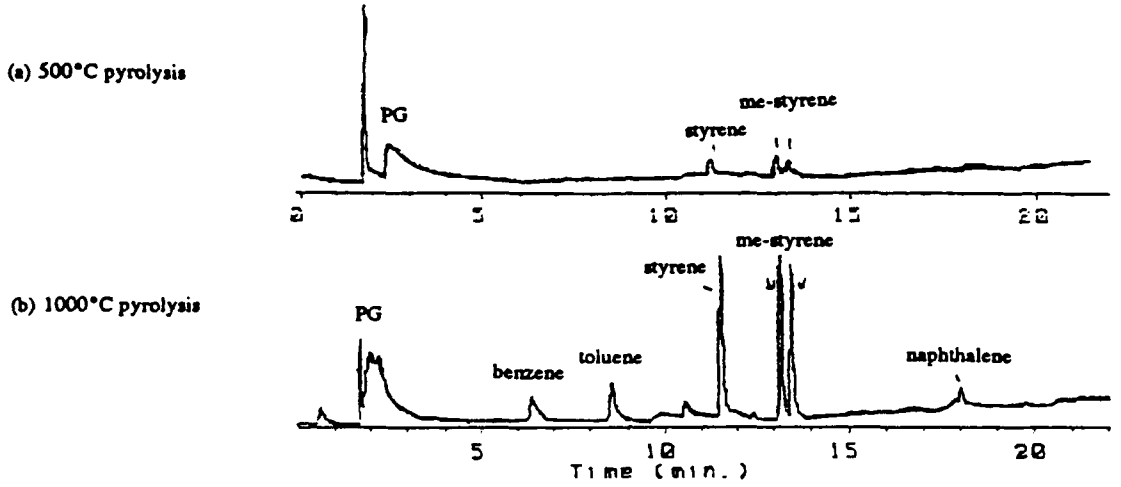



Figure 4. P-GC-FTIR Data for Unplasticized TPE Binder. (GC Injector Valve Opened at Initiation of Pyrolysis Pulse).

show two sharp, well-resolved peaks at 14 min and 15.6 min (peaks 13 and 14, respectively), whereas analyses performed on a surface that had been exposed to the atmosphere for 16 days following receipt of the samples do not show these peaks but do show two new peaks at 11 min and 17.5 min. The IR spectra of peaks 13 and 14 identify them as the nitrate esters plasticizers used in this formulation. Analyses of control samples confirm the assignment (chromatograms and spectra not shown). Spectra of peaks 9 and 11 identify them as esters (exact identity not yet determined). These desorption results suggest that nitrate ester plasticizer evaporated and/or decomposed while exposed to the atmosphere. Results from a previous investigation (Pesce-Rodriguez, Shaw, and Fifer 1991; Shaw and Fifer 1988) indicate that nitrate esters (or their decomposition products) may play a catalytic role in RDX decomposition. Depletion of plasticizer from HNIW-based propellant may therefore be very important. As a result of sample nonavailability, experiments on recently processed propellant ("Day 1" samples) were not reproduced; those of exposed ("Day 16" and older) samples were reproduced. Further desorption studies on freshly processed propellant are planned when samples become available.

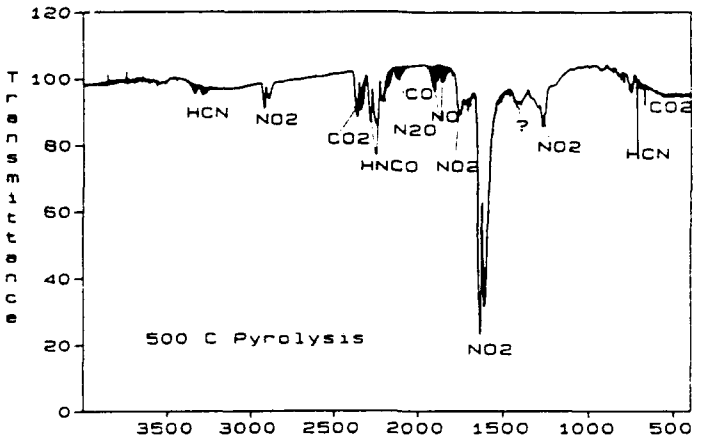
Comparison of the chromatograms obtained from HNIW/TPE pyrolysis experiments (Figures 3c–3g) with those of pure HNIW (Figures 2a–2e) indicates that the HNIW/TPE propellant and pure HNIW generate many of the same pyrolysis products (i.e., products 1–8 and 15). The HNIW/TPE formulation

differs from pure HNIW with respect to relative amounts of those products that it generates. Comparison of Figures 2b and 3d (500° C pyrolysis of 2-mg HNIW and the HNIW/TPE propellant, respectively) indicates that the propellant formulation generates relatively less product 4, 6, 7, and 8, relatively more product 1 (triazine), and approximately the same relative amounts of products 2, 3, and 5. In addition to the products common to HNIW and the propellant formulation, there are several products that are unique to the formulation and that do not appear to be related to the TPE binder (i.e., products 9–14). Products of the TPE binder are all benzene based (i.e., benzene, methyl benzene, styrene, methyl styrene, naphthalene) and do not appear in the pyrolysis product of the propellant formulations under any of the experimental conditions used in this investigation.

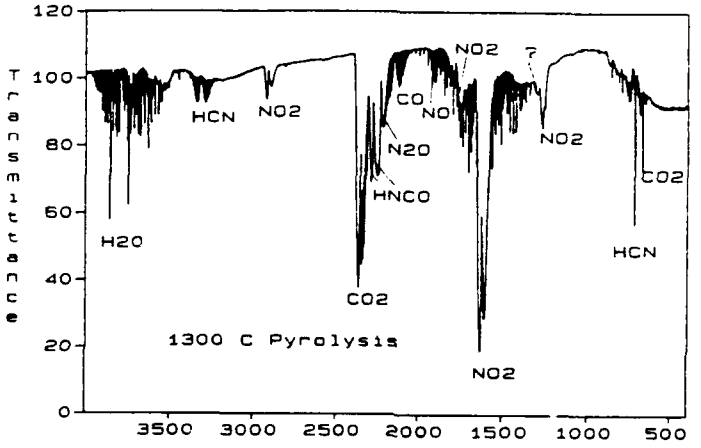
The significance of these observed similarities and differences in pyrolysis product generation has not yet been determined. It is suspected that propellant ingredients play a role in "removing" certain pyrolysis products by reacting with them to form nonvolatile residue or by catalyzing their conversion to permanent gases. Additional work on the exact identification of pyrolysis products and the elucidation of the mechanism of their formation and "removal" is currently in progress. Efforts will focus on examination of possible reactions between the plasticized binder, HNIW, and their respective decomposition products.

3.2 P-FTIR Spectroscopy. This technique generally detects small pyrolysis products, such as the permanent gases. Since no GC is involved, temporal information can be obtained if rapid scanning techniques are used (Patil, Chen, and Brill 1991). Experiments were carried out as a function of pyrolysis temperature (500° C and 1,300° C), atmosphere (air and $N_2$), and time (up to several minutes). Figures 5a and 5b show P-FTIR spectra for HNIW pyrolyzed at 500° C and 1,300° C, respectively. The spectra are similar, and show the presence of NO (1,800–1,950 $cm^{-1}$), $NO_2$ (~1,600 $cm^{-1}$ and weak bands at ~1,260 and 1,750 $cm^{-1}$), $N_2O$ (2,170–2,250 $cm^{-1}$), (CO 2,050–2,200 $cm^{-1}$), $CO_2$ (670 $cm^{-1}$, and 2,300–2,380 $cm^{-1}$), HNCO (2,220–2,300 $cm^{-1}$), HCN (720 $cm^{-1}$ and 3,220–3,380 $cm^{-1}$), plus bands near 1,300 $cm^{-1}$ and 1,410 $cm^{-1}$ due to additional pyrolysis products not yet identified. With increasing pyrolysis temperature, the $NO_2$ decreases slightly, and the $CO_2$ increases more noticeably, relative to the other products.

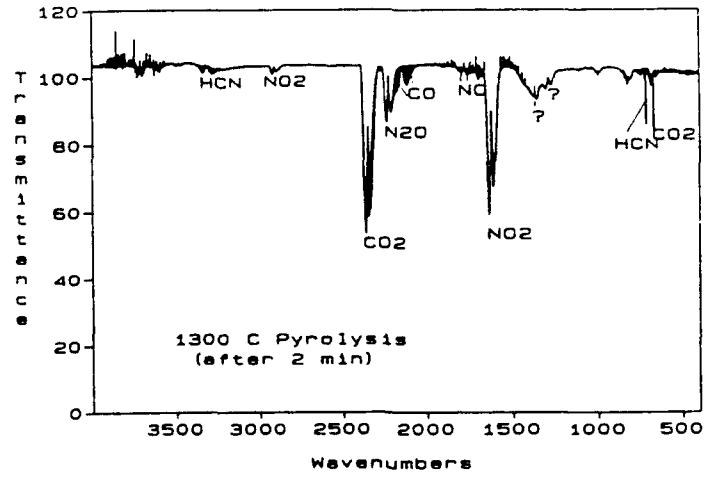
Use of rapid scanning P-FTIR techniques (Patil, Chen, and Brill 1991) to identify which products appear first has not yet been attempted. However, the observed changes in the composition of the pyrolysis products over a several second to several-minute time scale may be suggestive of secondary chemistry (on a much shorter time scale) during ignition and combustion. Figure 5c shows the FTIR spectrum corresponding to Figure 5b, several minutes after the pyrolysis. Taking into account the




(a)




(b)




(c)

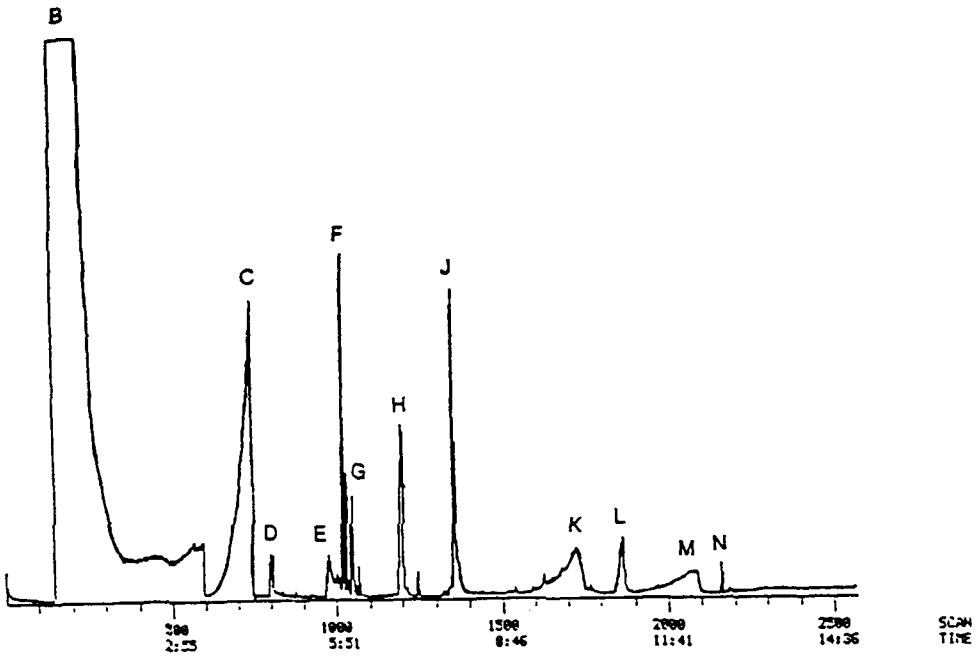
Figure 5. P-FTIR Data for HNIW.

difference in scale (ordinate axis), it can be seen that with time, the levels of HNCO, HCN, and $NO_2$ decrease and that new bands (as yet unassigned) near 1,350 $cm^{-1}$ appear.

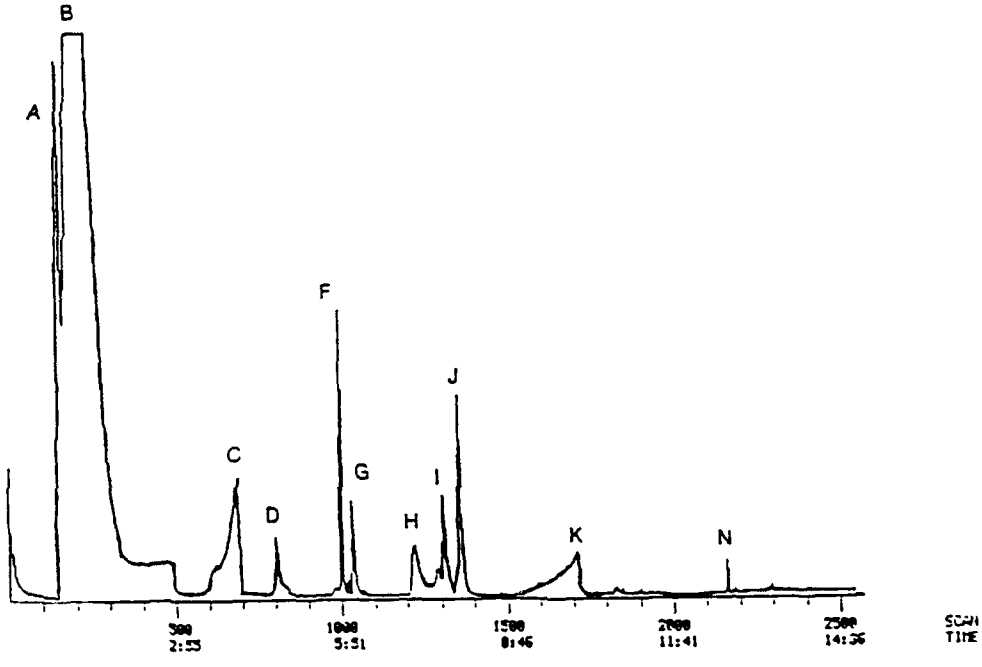
3.3 P-GC-MS. This is a well-established technique, and very sensitive to low-level nitramine pyrolysis products (Schroeder 1988, 1990a, 1990b). Figures 6a and 6b show representative total ion chromatograms for HNIW pyrolyzed at 500° C and 1,000° C, respectively. Although the chromatograms are very similar to each other, there are a few unique products at each temperature. In both cases, there is a very large peak at about 1 min due to small unseparated permanent gases (species are identified by associated mass spectra); in the 1,000° C run, this large peak is partially resolved by the cryogenic (−50° C) conditions into peak A, which is due to diatomic molecules (e.g., CO, NO, $N_2$), and peak B, which is much larger and is due to triatomic molecules (e.g., $N_2O$, $CO_2$) and $C_2N_2$. There is a medium intensity peak at 3 min due to $NO_2$ and several smaller peaks due to larger pyrolysis fragments. These peaks and principal masses in the corresponding mass spectra are summarized in Table 3.

In addition to the permanent gases, at least 12 other products are observed. Three of the products (E, L, M) are observed at 500° C but not at 1,000° C; one (I) is observed only at 1,000° C. As indicated in Table 3, many of the mass spectra were not present in the NIST library and have not yet been identified. There is evidence for cyanogen ($C_2N_2$, m/z 52) in the permanent gas peak, possibly from decomposition of HCN, which is observed under the tail of the permanent gas peak (e.g., scan 400–500). Formic acid (HCOOH), HNCO, and perhaps dimethyl formamide ($[CH_3]_2NCHO$, m/z 73) have also been identified. Although $NO_2$ frequently cannot be chromatographed, it appears to have been detected in this case. Products I and J are closely related to $NO_2$, both having m/z 46 and 30 as their two biggest fragments; although the presence of m/z 63 for Product J is consistent with nitric acid ($HNO_3$), the presence of m/z 28 and 44 fragments for products I and J is probably more consistent with $H_2NNO$ and $H_2NNO_2H$, respectively. Similarly, Products L and M appear to be structurally related, since both have similar mass spectra with m/z 96 as the predominant fragment. Product N produces fragments at m/z 149 and 177 and is the largest HNIW fragment observed in these experiments. Experiments using chemical- rather than electron-ionization are currently being performed. Results from these experiments should provide the molecular weight of each pyrolysis product as well as additional structural information from the CI fragmentation pattern.

Compared to HNIW, pyrolysis results for RDX and HMX at 500° C (chromatograms not shown) exhibit the following trends: HMX and RDX produce less $NO_2$ (as also observed with P-FTIR, see




(a)




(b)

Note: See Table 3 for mass spectral data for each product observed.

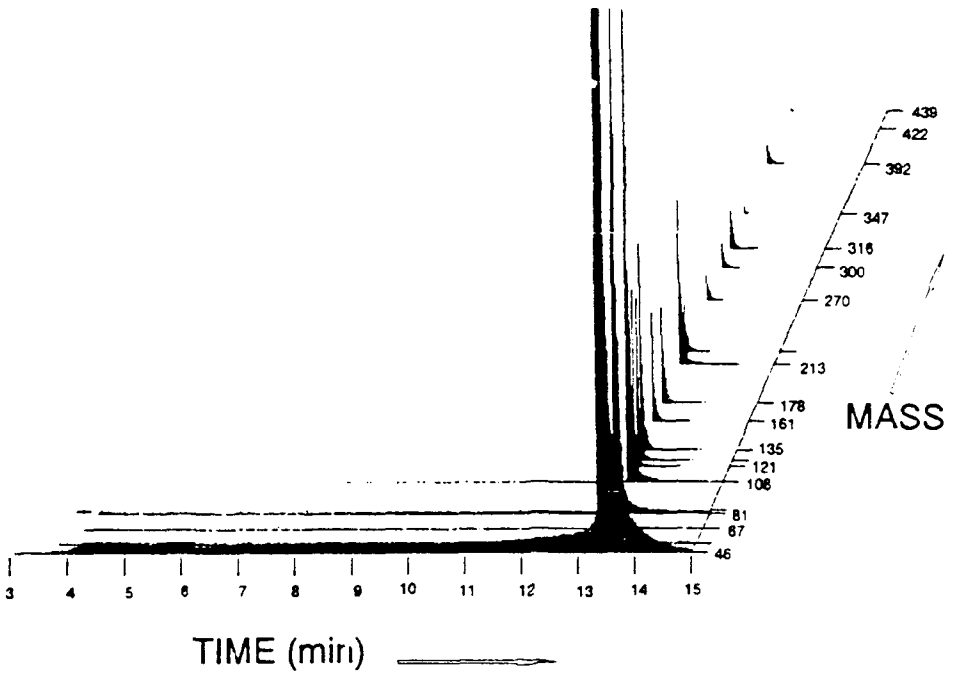
Figure 6. P-GC-MS Data for HNIW at (a) 500° C and (b) 1,000° C.

Table 3. Pyrolysis GC-MS Results for HNIW

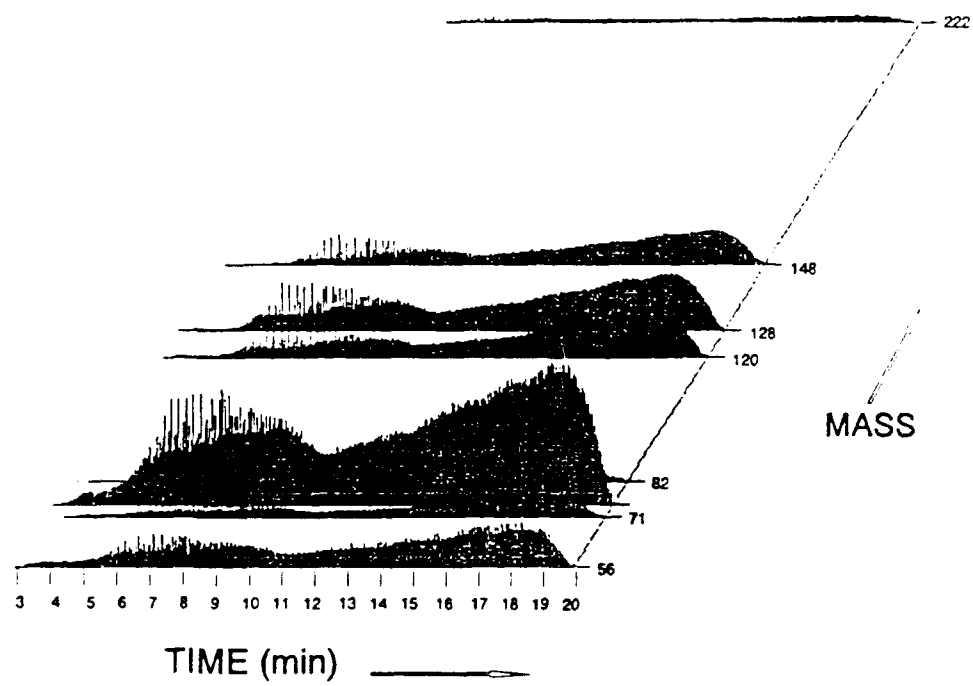
| Peak | Retention Time (min:sec) | Scan Number | Principal Masses (amu) | Identity | Comments |
|---|---|---|---|---|---|
| A | 0:55 | 156 | 30,44,28 | CO, $N_2$,NO,$CO_2$,$N_2O$ | |
| B | 1:15 | 215 | 44,30,28,52,26,45,46 | $CO_2$,$NO_2$,CO,NO,$C_2N_2$ | |
| C | 4:02 | 689 | 30,46 | $NO_2$ | |
| D | 4:41 | 802 | 43,42,29,28 | HNCO | |
| E | 5:44 | 982 | 70,40,43,28,29,30,42 | ? | 500° C only |
| F | 5:51 | 1,000 | 83,85,47,48,35,49,87 | ? | |
| G | 6:03 | 1,035 | 43,45,29,61,28,27,70,44,73,26,88 | ? | |
| H | 7:08 | 1,222 | 29,46,45,44,28 | HCOOH | |
| I | 7:39 | 1,309 | 46,30,28,44 | $H_2NNO$(?) | 1,000° C only |
| J | 7:55 | 1,360 | 46,30,44,28,63 | $H_2NNO_2H$(?),$HNO_3$(?) | |
| K | 10:00 | 1,713 | 45,29,44,28,43,73,96(?) | $(CH_3)_2NCHO$(?) | |
| L | 10:54 | 1,867 | 96,28,42,29,43,69,41,27,53,68 | ? | 500° C only |
| M | 12:10 | 2,083 | 96,28,42,43,27,30,41,46,69,45 | ? | 500° C only |
| N | 12:38 | 2,162 | 149,177,30,29,28,46,150,105,76 | ? | |

Section 3.2) and more of Product E. Under these conditions, the difference in observed HNCO between HNIW and RDX/HMX is not as large as in the P-FTIR experiments. Additional HNIW products common to RDX and HMX include H, J, K, and N. Several observed products are unique to HNIW, including F, G, I, L, and M.

3.4 P-MS Data. Figures 7a and 7b show the time evolution of the principal mass spectral peaks for HNIW and HMX, respectively, when heated isothermally below their normal decomposition temperature. The traces span a several-minute period. In these experiments, the sample is heated under vacuum conditions near the ionizing region of the MS; because of the vacuum conditions, vaporization as well as decomposition can occur. The behavior of the two nitramines is quite different. HMX (Figure 7b) appears to undergo both vaporization and decomposition, resulting in mass spectra that are invariant with time; the various humps in the selected ion traces result from amounts of the sample vaporizing at different times during the course of the analysis. The behavior for HNIW (Figure 7a) contrasts with that




(a)




(b)

Figure 7. P-MS Data: (a) HNIW at 210° C, (b) HMX at 250° C.

of HMX in that its mass spectra are observed to vary with time. In the early portion of the thermal treatment, species are evolved that give mass spectra having several mass fragments between the m/z range of 46 to 81. Approximately midway through the analysis, a fragment with m/z 108 appears in the mass spectrum. The mass spectrum remains fairly constant until rapid decomposition takes place near the end of the analysis. At that point, many larger fragments appear, including those with m/z as high as 392, 347, 316, 300, and 270. It is not clear to what extent this mass spectrum (shown in Figure 8) corresponds to pyrolysis fragments as opposed to ionization-induced fragments of vaporized HNIW. Very similar mass spectra are obtained for pyrolysis under programmed (30° or 60°/min) or pulsed (rapid heating to 1,000° C) conditions; this, together with the rapid gasification late in the isothermal run (Figure 7a) suggests that pyrolysis, rather than just vaporization, is taking place. The mass spectrum shown in Figure 8 exhibits no significant intensity at m/z 438, the molecular weight of HNIW, but it is common not to observe a parent peak when using 70-eV electrical ionization. The largest fragment with significant intensity has an m/z of 392, which corresponds to loss of one $NO_2$ from the HNIW molecule.

3.5 Extinguished Propellant Studies. Figure 9 gives the FTIR-photoacoustic (FTIR-PA) spectra of HNIW (Figure 9a), unplasticized TPE binder (Figure 9b), a hand-mixed propellant (Figure 9c), and the surface of the hand-mixed propellant after burning and extinguishment (Figure 9d). In the spectrum of the unburned propellant (Figure 9c), features of both HNIW and the TPE are visible. Comparison of these features in spectra (c) and (d) suggest that the surface of the extinguished propellant is slightly enriched in TPE (e.g., compare intensity of RDX band near 3,050 $cm^{-1}$ with that of HNIW near 2,900 $cm^{-1}$ in Figures 9c and 9d). This phenomenon has been observed in the spectra of several other extinguished propellants (Schroeder et al. 1991). Examination of the residue that bleeds from the burning HNIW/TPE grain was performed by IR microscopy (spectrum not shown) and found to be composed primarily of the HYTREL TPE.

Unfortunately, this hand-mixed HNIW/TPE propellant contained only about 60% HNIW and therefore burned with formation of large amounts of surface char, making it unsuitable for more detailed extinguished propellant studies. Scanning electron microscope (SEM) analysis of a cryogenically cleaved extinguished sample showed a very thin reaction/melt layer.

Attempts at burning/extinguishing the Thiokol HNIW/TPE formulation were unsuccessful due to the rapid and nearly complete combustion of the propellant, leaving no sample for subsequent analysis.

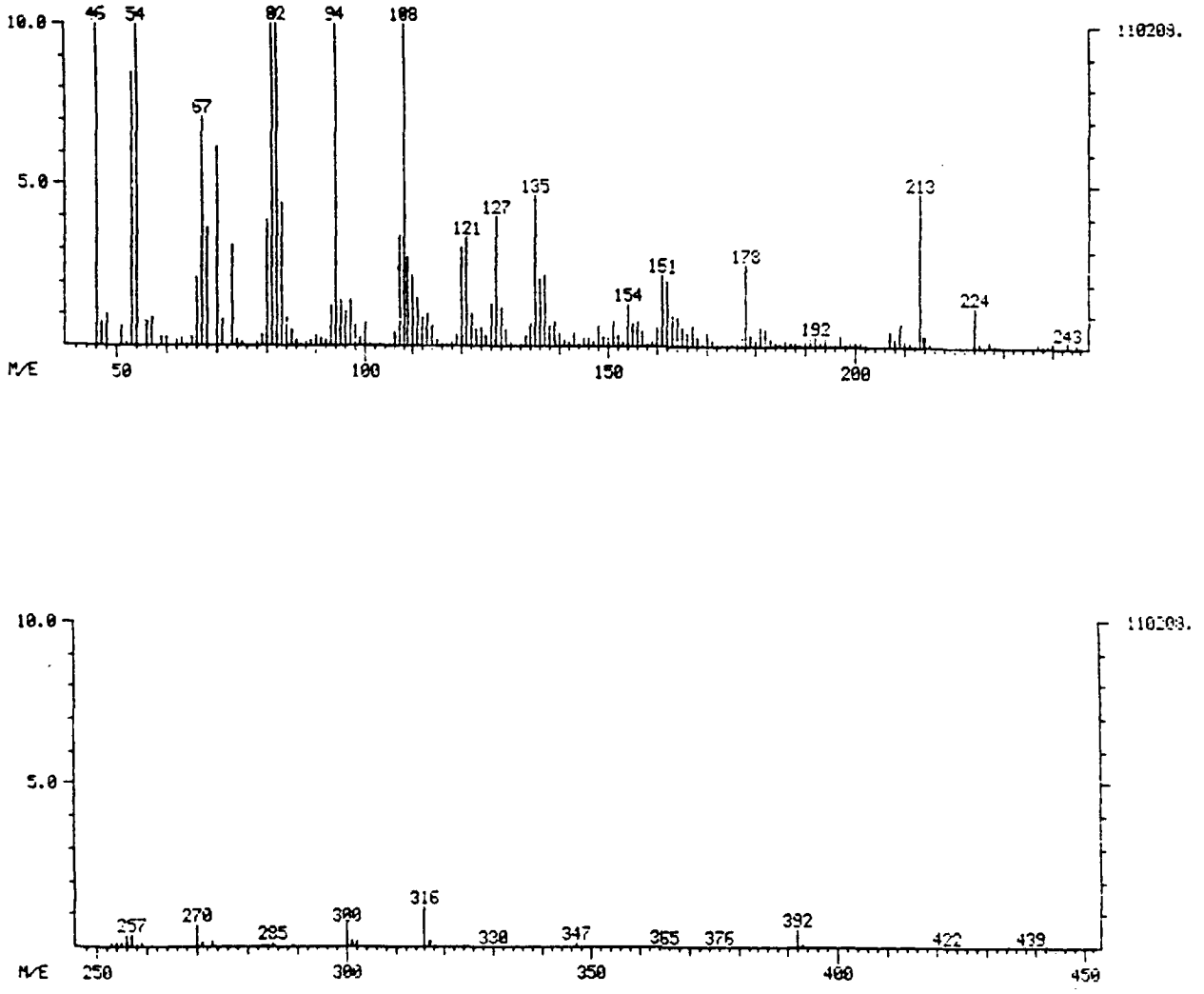



Figure 8. Mass Spectrum of HNIW During Late Stages of Pyrolysis.

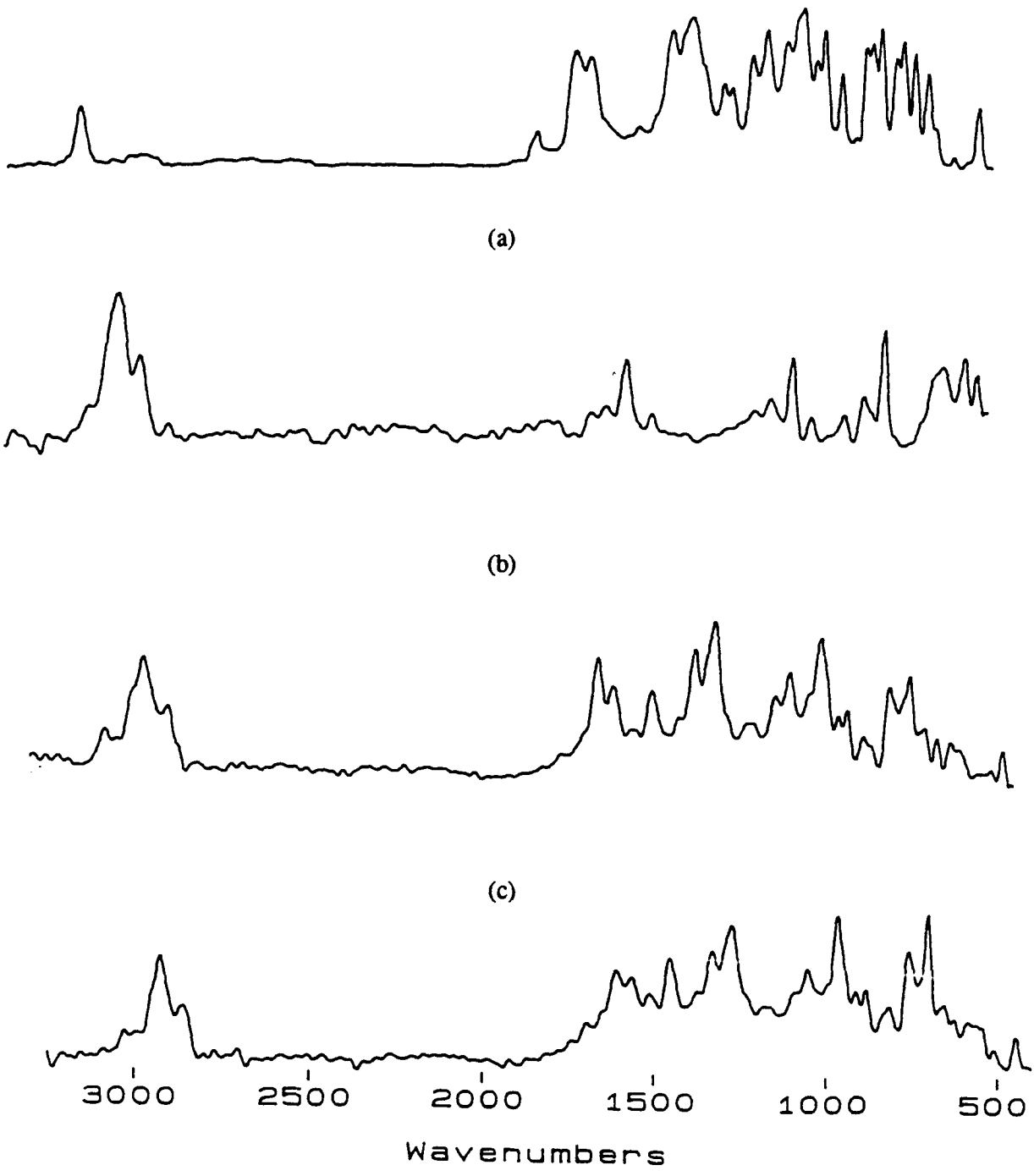



Figure 9. Photoacoustic FTIR Spectra: (a) HNIW, (b) Unplasticized TPE, (c) Hand-Mixed Unplasticized HNIW/TPE Propellant, (d) Extinguished Surface of Sample in (c).

## 4. SUMMARY AND FUTURE WORK

Both permanent gas and large fragment pyrolysis products of HNIW have been examined by P-FTIR, P-GC-MS, and P-GC-FTIR techniques and the results compared to those for HMX and RDX. HNIW produces a higher $CO_2$:$N_2O$ ratio than do RDX and HMX. In addition to two unique large pyrolysis products (i.e., N-C heterocycles), HNIW generates several of the same products as RDX and HMX, including triazine and formic acid, as well as an unidentified ester, ketone and isocyanate.

Investigation of the effect of propellant ingredients suggests the "removal" of HNIW decomposition products by reaction with either the TPE binder or the nitrate ester plasticizers (or their decomposition products). Desorption studies appear to indicate evaporation and/or decomposition of nitrate ester plasticizers from "aged" HNIW/TPE propellant formulations.

Variations in pyrolysis product distributions as a function of sample size are suspected to result from secondary reactions of HNIW and/or its decomposition products. Further analysis of "large" samples is being conducted to determine the reactants and mechanisms of these secondary reactions.

Future work will include: (a) correlation and identification of the large pyrolysis fragments observed with the P-GC-FTIR and P-GC-MS techniques; (b) further measurements on extinguished HNIW propellants, including identification of subsurface combustion products using HPLC-MS, in order to formulate a mechanism for the thermochemistry of HNIW during ignition and combustion; (c) examination of solution-phase thermochemistry of HMX, RDX, and HNIW, using supercritical fluid solvents; and (d) investigation of evaporation and/or decomposition of nitrate ester plasticizers in "aged" HNIW/TPE formulations.

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# APPENDIX:

# GAS PHASE FTIR SPECTRA OF PYROLYSIS PRODUCTS OF HNIW AND THE HNIW/TPE PROPELLANT

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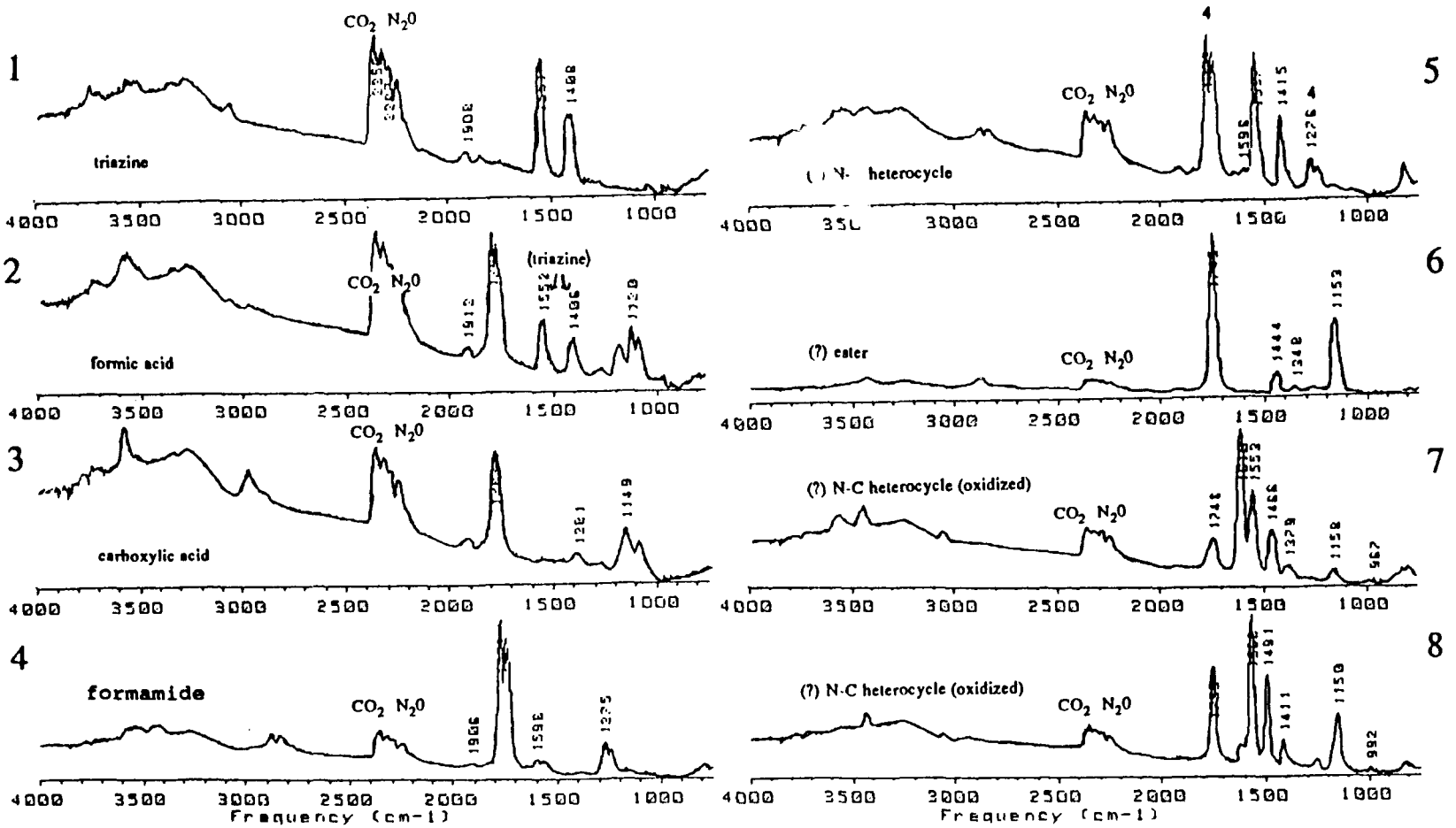


Figure A-1. Gas Phase FTIR Spectra of Pyrolysis Products of HNIW and the HNIW/TPE Propellant.

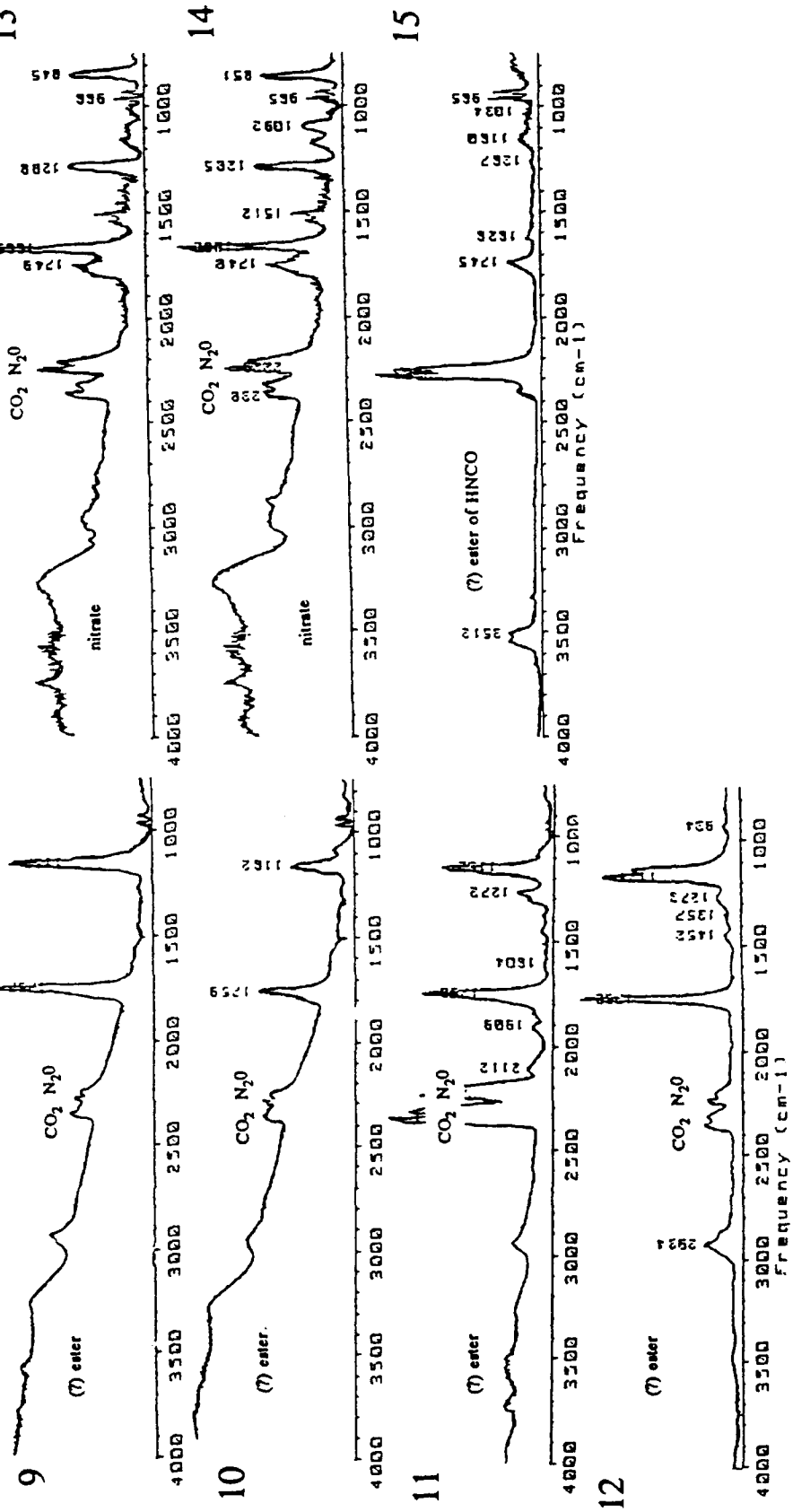


Figure A-1 (cont). Gas Phase FTIR Spectra of Pyrolysis of HNIW and the HNIW/TPE Propellant.

Table A-1. Pyrolysis Products of HNIW and/or HNIW/TPE Formulation

| Peak Number | Retention Time (min) | Identification |
|---|---|---|
| 1 | 7.5 | triazine |
| 2 | 10.0 | formic acid |
| 3 | 12.8 | carboxylic acid |
| 4 | 12.5 | formamide |
| 5 | 14.9 | N-C heterocycle (?) |
| 6 | 15.0 | ester (?) |
| 7 | 17.0 | N-C heterocycle (oxidized)(?) |
| 8 | 19.0 | N-C heterocycle (oxidized)(?) |
| 9 | 12.7 | ester(?) |
| 10 | 16.7 | ester(?) |
| 11 | 17.6 | ester(?) |
| 12 | 19.0 | ester(?) |
| 13 | 13.8 | nitrate ester |
| 14 | 15.4 | nitrate ester |
| 15 | 16.5 | ester of HNCO |

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